(12) UK Patent Application (19) GB (11) 2 207 914 (13) A

(43) Application published 15 Feb 1989

(21) Application No 8718050

(22) Date of filing 30 Jul 1987

(71) Applicant
Davy McKee (London) Limited

(Incorporated in United Kingdom)

250 Euston Road, London, NW1 2PG

(72) Inventors
John Scarlett
Michael Anthony Wood

(74) Agent and/or Address for Service
Batchellor Kirk & Eyles
2 Pear Tree Court, Farringdon Road,
London, EC1R 0DS

(51) INT CL⁴
C07C 31/20 C07D 307/08 307/32

(52) Domestic classification (Edition J):
C2C 1472 20Y 215 246 247 253 25Y 304 305 30Y 351 352 360 361 36Y 386 401 40Y 503 50Y 569 607 625 633 69Y 761 767 TV VQ YN ZN

(56) Documents cited
None

(58) Field of search
C2C

(54) **Process for the production of a mixture of butane 1,4-diol gamma-butyrolactone and tetrahydrofuran**

(57) A process for the production from a hydrocarbon feedstock selected from C_4 and C_6 hydrocarbons of a mixture of butane-1,4-diol, *gamma* -butyrolactone, and tetrahydrofuran comprises catalytically oxidising the hydrocarbon feedstock to form maleic anhydride and an acidic residue comprising a mixture of maleic acid and fumaric acid, reacting said acidic residue with an alkanol in one or more stages to form a diester mixture comprising a mixture of dialkyl maleate and dialkyl fumarate, and hydrogenating at least the dialkyl maleate component of said diester mixture to form a mixture of butane-1,4-diol, *gamma* -butyrolactone, and tetrahydrofuran.

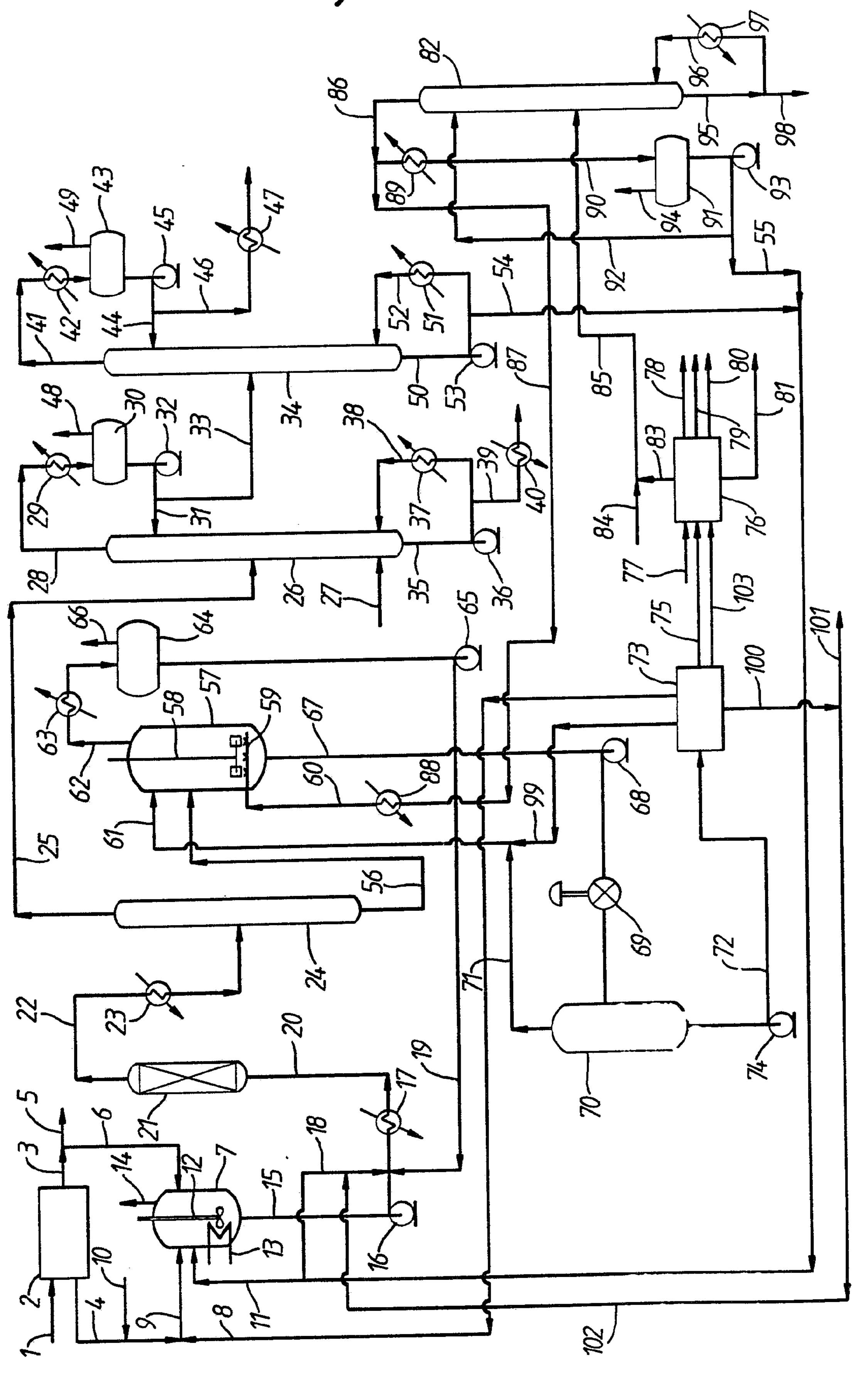
The drawing(s) originally filed was (were) informal and the print here reproduced is taken from a later filed formal copy

The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1982

GB 2 207 914 A

2207914

1/1



PROCESS

This invention relates to a process for the production of a mixture of butane-1,4-diol, *gamma*-butyrolactone and tetrahydrofuran from a hydrocarbon feedstock.

A process has been described for the production of butane-1,4-diol, tetrahydrofuran and *gamma*-butyrolactone by hydrogenation of dialkyl maleates in the vapour phase in at least two hydrogenation zones (see EP-A-0143634, WO-A-86/03189 and WO-A-86/07358). Continuous production of dialkyl maleates for use in this process is described in copending British Patent Application No. 8618888 filed 1st August 1986. Flowsheets of a complete plant for producing butane-1,4-diol, *gamma*-butyrolactone and tetrahydrofuran from maleic anhydride are described in British Patent Applications Nos. 8618889 and 8618894 filed 1st August 1986.

Maleic anhydride for use as feedstock in the production of dialkyl maleates can be produced by vapour phase oxidation of benzene in the presence of a catalyst, such as a supported vanadium pentoxide catalyst promoted with MoO_3 and possibly other promoters. Another hydrocarbon feedstock used for maleic anhydride is a mixed butylenes feedstock. This can be oxidised to maleic anhydride using a catalyst, such as vanadium pentoxide supported on alumina and activated with phosphorus pentoxide. There are many disclosures in the patent literature of processes of this type for production of maleic anhydride from a variety of hydrocarbon feedstocks.

In the production of maleic anhydride it is essentially unavoidable to produce an acidic by-product stream which consists mainly of maleic acid and fumaric acid. Although some further maleic anhydride can be produced from such by-product streams by dehydration and

cyclisation, it is normally uneconomic to do so. Hence it is usual practice to regard such by-product streams as waste products and to burn them.

It would be desirable to find a use for the acidic by-product stream from a maleic anhydride plant.

The present invention accordingly seeks to provide a useful way of utilising the acidic by-product stream from a maleic anhydride production plant. It further seeks to provide a process for the production from a hydrocarbon feedstock of butane-1,4-diol, _gamma_-butyrolactone and tetrahydrofuran.

According to the present invention there is provided a process for the production from a hydrocarbon feedstock selected from C_4 and C_6 hydrocarbons of a mixture of butane-1,4-diol, _gamma_-butyrolactone, and tetrahydrofuran which comprises catalytically oxidising the hydrocarbon feedstock to form maleic anhydride and an acidic residue comprising a mixture of maleic acid and fumaric acid, reacting said acidic residue with an alkanol in one or more stages to form a diester mixture comprising a mixture of dialkyl maleate and dialkyl fumarate, and hydrogenating at least the dialkyl maleate component of said diester mixture to form a mixture of butane-1,4-diol, _gamma_-butyrolactone, and tetrahydrofuran.

The invention further provides a process for the production of a mixture of butane-1,4-diol, _gamma_-butyrolactone and tetrahydrofuran which comprises esterifying an acidic residue containing a mixture of maleic acid and fumaric acid in one or more stages by reaction with an alkanol to form a diester mixture comprising dialkyl maleate and dialkyl fumarate, and hydrogenating at least the dialkyl maleate component of said diester mixture to form a mixture of butane-1,4-diol, _gamma_-butyrolactone, and tetrahydrofuran.

The alkanol is preferably a C_1 to C_4 alkanol.

It is preferably selected from methanol, ethanol, *n*-propanol, *iso*-propanol, *n*-butanol and *iso*-butanol. The preferred alkanol is ethanol.

Esterification is preferably effected in two or more stages. In a preferred process the acidic residue is reacted with said alkanol in a monoesterification zone to form a corresponding monoester mixture comprising monoalkyl maleate and monoalkyl fumarate, followed by reaction of resulting monoester mixture with further alkanol to form a diester mixture comprising dialkyl maleate and dialkyl fumarate, and the process includes the steps of supplying a first liquid feed comprising said monoester mixture to a secondary esterification zone containing a charge of a solid esterification catalyst, supplying a second feed stream comprising said alkanol to said secondary esterification zone, maintaining said secondary esterification zone at an elevated temperature sufficient to form or to maintain therein a vaporous stream containing said alkanol, intimately contacting said first liquid feed in said secondary esterification zone in the presence of said catalyst with said vaporous stream, recovering from said secondary esterification zone a vaporous effluent stream containing, in addition to alkanol vapour, also water in vapour form, said water being produced in said secondary esterification zone by esterification of said monoester mixture with said alkanol, and recovering from said secondary esterification zone a liquid stream containing said diester mixture.

In the process of the invention the acidic residue can be at least partly replaced or supplemented by maleic anhydride. The source of the acidic residue can be a maleic anhydride plant utilising a C_4 or C_6 hydrocarbon feedstock adjacent and connected to the esterification section of the plant. Alternatively the acidic residue can be imported by tanker or pipeline to the site from a

distant maleic anhydride plant.

Typically the acidic residue has a composition which comprises maleic acid and fumaric acid in an approximately 1:1 molar ratio. However this ratio can vary from about 1:10 to about 10:1.

A single secondary esterification zone may be used; however, it is also possible to use a plurality of secondary esterification zones connected in series.

The first liquid feed supplied to the secondary esterification zone (or to the first of the secondary esterification zones, if two or more such zones in series are used) contains a mixture of monoalkyl maleate and monoalkyl fumarate. Preferably the first liquid feed to the secondary esterification zone (or to the first such zone, if more than two secondary esterification zones are used) comprises a mixture of monoesters (i.e. monoalkyl maleate and monoalkyl fumarate) and diesters (i.e. dialkyl maleate and dialkyl fumarate). Such a mixture can be obtained by passage of the monoesterification product mixture, possibly after admixture of further alkanol therewith, through a primary esterification zone containing a charge of a solid esterification catalyst, such as an ion exchange resin containing acidic substituents selected from sulphonic acid groups and carboxylic acid groups. By passage of a mixture of monoalkyl maleate, monoalkyl fumarate, and alkanol therethrough in co-current, at least a proportion of the monoalkyl maleate and monoalkyl fumarate is converted in such a primary esterification zone to dialkyl maleate and dialkyl fumarate. In this case at least a major part of the water of esterification present in the primary esterification product is preferably removed therefrom, for example by distillation, to yield an ester feedstock which can be used as the first liquid feed to the secondary esterification zone, or to the first of a

plurality of such zones connected in series.

It will be seen that water of esterification is removed as vapour from the, or from each, secondary esterification zone by stripping with a stream of alkanol vapour. The second feed stream comprising said alkanol can be supplied in liquid form to the or each secondary esterification zone and vaporised therein. Often however, it is supplied thereto in vapour form.

The or each secondary esterification zone can be operated in batch mode. For large scale production, however, it will more usually be operated continuously; in this case said first liquid feed is continuously supplied to the or each secondary esterification zone and said liquid product is continuously recovered therefrom.

The rate of supply of the second feed stream comprising said alkanol as, or to form, the vaporous stream in the or each secondary esterification zone should be such as to establish and maintain a sufficient concentration of reactant alkanol in the liquid phase to drive the mono- to dialkyl maleate and fumarate esterification reactions towards completion and to strip a major part, preferably substantially all, of the water of esterification released by means of these reactions in the respective secondary esterification zone from the liquid phase. The lower the concentration of water in the second feed stream is, the more efficient will be the degree of stripping of product water from the respective secondary esterification zone and the higher will be the conversion to dialkyl maleate and dialkyl fumarate. If a second feed stream comprising "dry" alkanol is used with a water content of, for example, about 1 mole % or less, then it is possible to operate the process so that the liquid product stream comprises at least about 95 mole % of a mixture of dialkyl maleate and dialkyl fumarate, and often at least about 97 mole %, e.g. 99 mole % or more, of a

mixture of dialkyl maleate and dialkyl fumarate. On the other hand, if the water content of the second feed stream is in the region of about 10 mole %, then the diester content of the liquid product stream will be correspondingly lower, e.g. about 80 mole % up to about 85 mole %.

If a mixture of acidic residue and maleic anhydride is used, this preferably contains at least about 50 mole % of acidic residue and not more than about 50 mole % of maleic anhydride. However a mixture of up to 90 mole % maleic anhydride and not more than about 10 mole % of acidic residue can also be used in the process of the invention. The higher the acid residue content is, the larger is the amount of water that will be produced in the monoesterification zone.

As a heterogeneous esterification catalyst is used, the catalyst remains in the or each secondary esterification zone. Thus the liquid product therefrom is essentially free from sulphurous impurities introduced as a result of interaction with the catalyst and can be subjected to conventional distillation or similar techniques in order to recover diester mixture without having to neutralise the catalyst.

In one preferred process the second feed stream to the secondary esterification zone, if there is only one such zone, or to the final secondary esterification zone, if more than one such zone is used, contains less than about 1 mole % of water.

The monoesterification step can be effected as a batch process but is preferably conducted as a continuous process. In the monoesterification step the temperature is typically from about 50°C to about 150°C, e.g. about 60°C to about 100°C, while the pressure is sufficient to maintain the alkanol in the liquid phase. Typically this is in the range of from about 1 bar up to about 5 bar

absolute.

The monoesterification zone may comprise any convenient form of reactor, e.g. a stirred tank reactor. The reaction mixture is generally retained in the monoesterification zone for a predetermined time, typically of the order of from about 15 minutes to about 300 minutes or more, e.g. about 60 minutes. The residence time is selected to permit substantially complete reaction of maleic acid and fumaric acid, as well as of any maleic anhydride present, with the alkanol under the chosen reaction conditions to form the monoester mixture. Hence the reaction mixture from the monoesterification zone comprises monoalkyl maleate, monoalkyl fumarate, usually also excess alkanol, besides possibly also some water, maleic anhydride, dialkyl maleate, dialkyl fumarate, maleic acid, and fumaric acid.

This monoesterification mixture is passed forward for catalytic conversion to the corresponding diester mixture, possibly after addition of further alkanol. These diesterification reactions are equilibrium reactions. Hence, in order to maximise production of diesters, it is necessary to remove the water formed in the esterification reactions.

In a preferred continuous process according to the invention a first liquid feed stream containing a mixture of monoalkyl maleate and monoalkyl fumarate is passed through at least one secondary esterification zone and is intimately contacted therein with a stream of alkanol vapour in the presence of a solid esterification catalyst. The first liquid feed stream to the secondary esterification zone, if there is only one such zone, or to the first secondary esterification zone, if there are two or more such zones, will usually be a mixed feed stream containing monoalkyl maleate, monoalkyl fumarate, dialkyl maleate and dialkyl fumarate; such a mixed feed stream can

be obtained by passing a mixture of monoalkyl maleate, monoalkyl fumarate and alkanol, usually in molar excess of that required to effect esterification of the monoalkyl maleate and monoalkyl fumarate, in co-current through a primary esterification zone which contains a charge of a solid esterification catalyst and is maintained under esterification conditions. Such esterification conditions will normally include use of an elevated temperature in the intermediate esterification zone, as well as use of a pressure sufficient to maintain the alkanol in the liquid phase. The resulting primary esterification product mixture contains a mixture of mono- and dialkyl maleates and fumarates, typically in a monoester:diester mole ratio of from about 70:30 to about 20:80, in addition to excess alkanol and water produced in the esterification reactions. Preferably the residence time in the primary esterification zone is so selected in relation to the temperature and pressure conditions therein that the primary esterification product mixture is substantially an equilibrium mixture.

Examples of suitable solid esterification catalysts include ion exchange resins, preferably macroreticular ion exchange resins, containing sulphonic acid groups and/or carboxylic acid groups.

Typical reaction conditions in the primary esterification zone include use of a temperature in the range of from about 80°C to about 140°C, preferably about 100°C to about 125°C and of a pressure in the range of from about 1 to about 20 bar, preferably about 5 to about 15 bar. The liquid hourly space velocity through the primary esterification zone preferably ranges from about 0.25 hr^{-1} to about 5 hr^{-1}, typically about 1 hr^{-1} to about 2 hr^{-1}.

The primary esterification product mixture is free from added catalyst and hence can be distilled

without disturbing significantly the reaction equilibrium under normal, reduced or increased pressure, in order to separate alkanol and water, which are recovered overhead, from an ester-containing mixture containing both mono- and dialkyl maleates and fumarates. The ester-containing mixture resulting from distillation of the primary esterification product mixture can be used as such as the feed stream to the secondary esterification zone or can be admixed first with alkanol, with an inert diluent and/or with material recycled from downstream in the process.

The diester product mixture from the secondary esterification zone, if there is only one secondary esterification zone, or from the final secondary esterification zone, if there is more than one such zone, contains predominantly dialkyl maleate and dialkyl fumarate. The proportion of diester is, as already mentioned, dependent on the water content of the second feed stream. When a stream comprising "dry" alkanol containing, for example, less than about 1 mole % water is used as the second feed stream, then the liquid product stream from the secondary esterification zone, if there is onl one such zone, or from the final secondary esterification zone, if there is more than one such zone, typically contains diesters (i.e. dialkyl maleate and dialkyl fumarate) in an amount of at least about 97 mole % up to about 99 mole % or more, as well as alkanol, and small amounts of water, maleic acid, fumaric acid, monoalkyl maleate and monoalkyl fumarate. This diester product mixture can be distilled to produce a diester rich product which is free from catalyst. This catalyst free diester product can be further purified, e.g. by subjection one or more times to the process of British Patent Application No. 8618892 filed 1st August 1986. If desired, the purification steps may include washing with aqueous alkali or, preferably, with an aqueous wash liquor

which contains an alkali metal hydroxide, carbonate, bicarbonate, or a mixture of two or more thereof dissolved in an aqueous solution of the corresponding di-(alkali metal) salt of maleic acid according to the teachings of copending British patent Application No. 8618893 filed 1st August 1986 and then with water, followed by one or more distillation steps.

The preferred alkanol is ethanol and the preferred diesters are diethyl maleate and diethyl fumarate.

The cost of producing "dry" ethanol from a "wet" ethanol stream is appreciable. Moreover, it will usually be desirable upon economic grounds to recycle ethanol present in the vaporous effluent stream from the, or from each, secondary esterification zone and in other available streams, for example from a downstream hydrogenation step utilising the process of EP-A-0143634, of WO-A-86/03189 or of WO-A-86/07358, for production of further diethyl maleate. Hence in some cases it may be decided that it is uneconomic to produce "dry" ethanol, e.g. with a water content of no more than about 1 mole %. In this case available ethanol-containing streams may contain from about 2 mole % up to about 10 mole % or more, e.g. up to about 15 mole % of water. Such ethanol containing streams can be utilised as the second feed stream but in this case it will usually suffice to utilise a single secondary esterification zone, e.g. a stirred tank reactor, containing a charge of an ion exchange resin containing sulphonic acid and/or carboxylic acid groups. The diester (i.e. diethyl maleate and diethyl fumarate) content of the liquid product stream will in this case usually be significantly lower than in the case where "dry" ethanol is used. Hence, under these circumstances, the diester content of the liquid product may be from about 75 mole %, usually at least about 80 mole %, up to about 85 mole % or

so, and typically not more than about 90 mole %.

When a stream comprising "wet" ethanol is used as the second feed stream, for example a stream containing from 2 mole % up to about 10 mole % water, then the final product mixture may contain, for example, from about 75 mole % up to about 90 mole %, e.g. about 80 mole % to about 85 mole %, diesters (i.e. dialkyl maleate and dialkyl fumarate) with the balance comprising monoalkyl maleate, monoalkyl fumarate, water, maleic acid, and fumaric acid. Advantageously such a liquid product stream is further purified by the process of British Patent Application No. 8618892 filed 1st August 1986.

In a preferred process, acidic residue, possibly also maleic anhydride, and ethanol, preferably in molar excess, are reacted in the monoesterification zone to yield a mixture of monoethyl maleate, monoethyl fumarate and ethanol. This is preferably admixed with a further quantity of ethanol and passed to a primary esterification zone, which contains a charge of a solid esterification catalyst, such as an ion exchange resin of the type mentioned above. The primary esterification zone can take the form of a trickle bed reactor or a stirred tank reactor or a resin packed column.

The resulting mixture of monoethyl maleate, monoethyl fumarate, diethyl maleate, diethyl fumarate, ethanol and water (and possibly also minor amounts of impurities) is then distilled in a first distillation zone to yield an ethanol/water mixture, containing also a minor amount of diesters (i.e. diethyl maleate and diethyl fumarate), as overhead product, and an ester-containing product containing, typically, an approximately 70:30 molar mixture of diesters (i.e. diethyl maleate and diethyl fumarate) and monoesters (i.e. monoethyl maleate and monoethyl fumarate) plus a small amount of "light ends", such as ethanol and water, as a bottom product.

Distillation is preferably effected under flash distillation conditions. It can be carried out under reduced pressure, e.g. at about 0.5 bar. As it is not necessary to remove all of the "light ends" from the bottom product, the bottom of the first distillation zone can be kept relatively cool thus reducing the risk of thermal decomposition at this stage.

The overhead product from the first distillation zone is, as already noted, a mixture of water and ethanol (plus a minor amount of diesters); if desired, the monoester:ethanol molar ratio of the reactant mixture fed to the primary esterification zone is so controlled that the water content of the overhead product from this distillation step is higher than the water/ethanol azeotrope obtained upon distillation of water/ethanol mixtures at the pressure of distillation. This mixture can then be redistilled in a second distillation zone, again conveniently at or just above atmospheric pressure, to yield a "wet" ethanol overhead product which is drier than the feed to the second distillation zone but is still wetter than the water/ethanol azeotrope obtainable upon distillation of water/ethanol mixtures at the pressure of the second distillation zone. The "wet" ethanol overhead product from the second distillation zone typically contains about 15 mole % of water. Part of this "wet" ethanol overhead product from the second distillation zone can be recycled to the intermediate esterification zone while part is returned to the second distillation zone as a reflux stream, and the remainder is passed to an ethanol dehydration unit to produce "dry" ethanol to form the vaporous feed stream in the secondary esterification zone, if there is only one such zone, or to the final secondary esterification zone, if there is more than one such zone. The bottom product from the second distillation zone is mainly water but contains any diethyl maleate and diethyl

fumarate that distils from the first distillation zone.

The ethanol dehydration unit may be of any suitable design capable of producing from a "wet" ethanol stream containing up to about 20 mole % water a sufficient stream of "dry" ethanol with a water content less than about 1 mole % for use as the source of the vaporous feed stream in the secondary esterification zone. Membrane separation techniques can be used for the production of "dry" ethanol; alternatively molecular sieves can be used.

In one preferred form of the process a single secondary esterification zone is used which may comprise a stirred tank reactor containing a charge of a macroreticular ion exchange resin containing sulphonic acid groups, such as Amberlyst 16, through which ethanol vapour is bubbled.

Following purification of the diester mixture by removal of traces of acidic materials therefrom, for example by the process of British Patent Application No. 8618892 filed 1st August 1986, the diester mixture can be separated by distillation to yield a pure diethyl maleate stream which can be used as described in copending British Patent Application No. 8618890 filed 1st August 1986 for separation of _gamma_-butyrolactone product from diethyl succinate formed as by-product in the hydrogenation step. Such diethyl maleate can also be used as feedstock for the hydrogenation step. From the distillation of the purified diester mixture there is also obtained a diethyl fumarate rich stream; this can be passed to the hydrogenation step as it is equally suitable for use as a feedstock therein.

Hydrogenation can be effected as described in EP-A-0143634, in WO-A-86/03189 or in WO-A-86/07358. Recovery of butane-1,4-diol, _gamma_-butyrolactone and tetrahydrofuran from the C_4 product mixture from the hydrogenation step can be effected using the process described in British Patent Application No. 8618890 filed

1st August 1986, and/or by the process described in British Patent Applications Nos. (Case 87125), (Case 87167), (Case 87158), and/or (Case 87147) filed 29th July 1987. The disclosures of all copending applications referred to herein are hereby incorporated by reference.

In order that the invention may be clearly understood and readily carried into effect a preferred form of plant for the production of a mixture of butane-1,4-diol, gamma-butyrolactone, and tetrahydrofuran using a preferred process according to the invention will now be described, by way of example only, with reference to the accompanying drawing which is a flow diagram of the plant.

It will be understood by those skilled in the art that the drawing is diagrammatic and that further items of equipment such as reflux drums, pumps, vacuum pumps, temperature sensors, pressure sensors, pressure relief valves, control valves, flow controllers, level controllers, holding tanks, storage tanks, and the like would additionally be required in a commercial plant. The provision of such ancillary items of equipment forms no part of the present invention and is in accordance with conventional chemical engineering practice.

Referring to the drawing a C_4 hydrocarbon feedstock, e.g. a mixed butene feedstock, is supplied in line 1 to a conventional maleic anhydride plant 2 in which the feedstock is subjected to catalytic oxidation to form maleic anhydride, as the major product, in line 3 and an acidic residue containing a mixture of maleic acid and fumaric acid in an approximately 1:1 molar ratio in line 4. The maleic anhydride can be exported beyond plant limits in line 5 or can be passed by way of line 6 to monoesterification reactor 7. The acidic residue in line 4 is admixed with recycled material that contains recovered maleic anhydride and diethyl maleate in line 8

and the resulting combined stream in line 9 is fed to monoesterification reactor 7. Acidic residue from other sites can be brought to the plant and fed in line 10 to monoesterification reactor 7. Depending upon the market demands for maleic anhydride, for the C_4 products of the plant (i.e. butane-1,4-diol, gamma-butyrolactone and tetrahydrofuran), and on the availability of acidic residues from other plants so the proportions of materials fed in lines 4, 6 and 10 can be varied to suit the prevailing circumstances.

Monoesterification reactor 7 is also supplied with a stream containing ethanol in line 11. Monoesterification reactor 7 is provided with a stirrer 12, with a cooling coil 13 (which doubles as a steam heating coil at start up of the plant), and with a vent line 14. The acidic residue in line 4 and any maleic anhydride supplied in line 6 reacts with ethanol in reactor 7 to produce a mixture of monoethyl maleate and monoethyl fumarate in the absence of a catalyst. The liquid reaction mixture from reactor 7 is discharged in line 15 and pumped by pump 16 to steam heater 17. Upstream from heater 17 it is admixed with two streams comprising further ethanol supplied in lines 18 and 19. The mixed stream flows on in line 20 to a primary esterification reactor 21 which contains a fixed bed of an acidic ion exchange resin, such as Amberlyst 16. Reaction between monoethyl maleate and ethanol to form diethyl maleate takes place in reactor 21.

An intermediate esterification product mixture is recovered from primary esterification reactor 21 in line 22 and is heated by means of steam heater 23 before entering a flash distillation column 24. A vaporous stream containing mainly ethanol and water, but also a minor amount of diethyl ether (besides tetrahydrofuran and traces of diethyl maleate and diethyl fmarate, which are

present in a recycle stream to monoesterification reactor 7 as described further below), is recovered overhead in line 25 which leads to an ethanol recovery column 26. This is also supplied with water in line 27 which has been used in condensers in the plant and which includes water containing streams recovered from elsewhere in the plant. The overhead product from column 26 in line 28 is condensed by means of condenser 29 and contains mainly ethanol with lesser amounts of water, diethyl ether and tetrahydrofuran. The resulting condensate collects in drum 30; part is returned to column 26 in line 31 by pump 32 to form a reflux stream, whilst the remainder is passed in line 33 to an ether recovery column 34. A part of the bottom product from column 26 in line 35 is recycled by pump 36 to column 26 through column reboiler 37 and line 38. This bottom product in line 35 is mainly water but contains some ethanol and diethyl maleate. The remainder of the bottom product in line 35 is taken in line 39, cooled in cooler 40 and passed on to a water treatment plant (not shown).

From the ether recovery column 34 is recovered overhead in line 41 a vaporous stream comprising diethyl ether, together with minor amounts of ethanol, water and tetrahydrofuran. This is condensed by means of condenser 42. The resulting condensate collects in drum 43; part is recycled as a reflux stream to column 34 in line 44 by pump 45, while the remainder is passed in line 46 to cooler 47 and thence to storage.

Reference numerals 48 and 49 represent vent lines for condensate drums 30 and 43 respectively.

The bottom product from ether recovery column 34 in line 50 is mainly ethanol, but contains a minor amount of water and small amounts of tetrahydrofuran and diethyl ether. Part is returned through reboiler 51 in line 52 to column 34 by means of pump 53, whilst the remainder is

recycled in line 54 for admixture with further ethyl alcohol in line 55 to form the stream in line 11.

The bottom product from flash distillation column 24 is taken in line 56 to a secondary esterification reactor 57. This is provided with a stirrer 58 and a sparger 59 which is connected to a line 60 through which ethanol vapour is supplied to reactor 57. Further reaction of monoethyl maleate and monoethyl fumarate with ethanol occurs in reactor 57, resulting in formation of additional diethyl maleate and diethyl fumarate. A stream containing recycled ethanol is returned to reactor 57 in line 61.

Water of esterification is stripped by the upflowing ethanol vapour which exits reactor 57 in line 62. This vapour is condensed in condenser 63 and collects in drum 64 from which it is recycled to primary esterification reactor 21 in line 19 by pump 65. Reference numeral 66 represents a vent line for drum 64.

A liquid product mixture containing mainly diethyl maleate and diethyl fumarate but also lesser amounts of monoethyl maleate and monoethyl fumarate, together with some ethanol and water and traces of diethyl ether and tetrahydrofuran, is recovered in line 67. This is pumped by pump 68 through a pressure reduction valve 69 to a flash distillation column 70 which is operated under vacuum. The overhead stream in line 71 is recycled to secondary esterification reactor 57 by way of line 71 and contains ethanol and water besides some diethyl maleate and diethyl fumarate and traces of monoethyl maleate and monoethyl fumarate.

The bottom product from column 70 is pumped in line 72 to a diester purification plant 73 by pump 74. Plant 73 operates according to the teachings of British patent aplication No. 8618892 filed 1st August 1986. It preferably includes a distillation column for separation

of at least some of the diethyl maleate from diethyl fumarate. Acid free diester (i.e. diethyl maleate or a mixture of diethyl maleate and diethyl fumarate) is recovered in line 75 and is passed to a vapour phase hydrogenation plant 76. This is arranged to operate according to the process described in EP-A-0143634, in WO-A-86/03189 or in WO-A-86/07358 and is supplied with hydrogen in line 77. It includes a product recovery section, for example one designed to operate using acid free diethyl maleate for use in separation of gamma-butyrolactone and diethyl succinate according to the process of British patent application No. 8618890 filed 1st August 1986. There are recovered from plant 76 a stream of tetrahydrofuran in line 78, a stream of gamma-butyrolactone in line 79, and a stream of butane-1,4-diol in line 80. Minor amounts of "heavies" are recovered in line 81. A column 82 is fed with a mixture of "lights" recovered from plant 76, including ethanol and n-butanol, in line 83 and with make up ethanol in line 84. The mixed stream in line 85 yields upon distillation a vaporous stream in line 86 part of which flows on in line 87 through heater 88 and line 60 to the secondary esterification reactor 57. The rest of the vaporous stream in line 86 passes to a condenser 89. The resulting condensate in line 90 collects in drum 91, part being returned as a reflux stream to column 82 in line 92 by means of pump 93, and the remainder flowing in line 55 to join line 54. Reference numeral 94 indicates a vent line for drum 91. A stream of n-butanol, produced as a by-product in hydrogenation plant 76, is recovered from the bottom of column 82 in line 95. Part of this stream is returned to column 82 in line 96 through reboiler 97. the remainder is passed to storage in line 98.

From diester purification plant 73 there is recovered in line 99 a stream containing a mixture of

ethanol, diethyl maleate, diethyl fumarate, water, and maleic anhydride, besides traces of tetrahydrofuran, diethyl ether, maleic acid, and fumaric acid. This is admixed with the material in line 71 to form the stream in line 61. Also recovered from diester purification plant 73 is a stream containing maleic anhydride and diethyl maleate, besides traces of ethanol and water; this is recycled to monoesterification reactor 7 in line 11. Another stream recovered from plant 73 in line 100 contains a mixture of monoethyl maleate, monoethyl fumarate, diethyl maleate, and diethyl fumarate and minor amounts of "heavies". Part is purged in line 101, whilst the remainder is recycled to primary esterification reactor 21 in line 102.

If diester purification plant 73 includes a diethyl maleate/diethyl fumarate separation step to provide acid free diethyl maleate for use in separation of gamma-butyrolactone and diethyl succinate, then a diester stream containing diethyl fumarate can be passed to the hydrogenation section of plant 76 in line 103.

CLAIMS

1. A process for the production from a hydrocarbon feedstock selected from C_4 and C_6 hydrocarbons of a mixture of butane-1,4-diol, gamma-butyrolactone, and tetrahydrofuran which comprises catalytically oxidising the hydrocarbon feedstock to form maleic anhydride and an acidic residue comprising a mixture of maleic acid and fumaric acid, reacting said acidic residue with an alkanol in one or more stages to form a diester mixture comprising a mixture of dialkyl maleate and dialkyl fumarate, and hydrogenating at least the dialkyl maleate component of said diester mixture to form a mixture of butane-1,4-diol, gamma-butyrolactone, and tetrahydrofuran.

2. A process for the production of a mixture of butane-1,4-diol, gamma-butyrolactone and tetrahydrofuran which comprises esterifying an acidic residue containing a mixture of maleic acid and fumaric acid in one or more stages by reaction with an alkanol to form a diester mixture comprising dialkyl maleate and dialkyl fumarate, and hydrogenating at least the dialkyl maleate component of said diester mixture to form a mixture of butane-1,4-diol, gamma-butyrolactone, and tetrahydrofuran.

3. A process according to claim 1 or claim 2, in which the alkanol is a C_1 to C_4 alkanol.

4. A process according to claim 3, in which the alkanol is ethanol.

5. A process according to any one of claims 1 to 4, in which the acidic residue is at least partly replaced or supplemented by maleic anhydride.

6. A process according to any one of claims 1 to 5, in which the acidic residue has a composition which comprises maleic acid and fumaric acid in a molar ratio of from about 1:10 to about 10:1.

7. A process according to any one of claims 1 to 6, in which esterification is effected in two or more stages.

8. A process according to any one of claims 1 to 7, in which the acidic residue is reacted with said alkanol in a monoesterification zone to form a corresponding monoester mixture comprising monoalkyl maleate and monoalkyl fumarate, followed by reaction of resulting monoester mixture with further alkanol to form a diester mixture comprising dialkyl maleate and dialkyl fumarate, and which further includes the steps of supplying a first liquid feed comprising said monoester mixture to a secondary esterification zone containing a charge of a solid esterification catalyst, supplying a second feed stream comprising said alkanol to said secondary esterification zone, maintaining said secondary esterification zone at an elevated temperature sufficient to form or to maintain therein a vaporous stream containing said alkanol, intimately contacting said first liquid feed in said secondary esterification zone in the presence of said catalyst with said vaporous stream, recovering from said secondary esterification zone a vaporous effluent stream containing, in addition to alkanol vapour, also water in vapour form, said water being produced in said secondary esterification zone by esterification of said monoester mixture with said alkanol, and recovering from said secondary esterification zone a liquid stream containing said diester mixture.

9. A process according to claim 8, in which a single secondary esterification zone is used.

10. A process according to claim 8, in which a plurality of secondary esterification zones connected in series is used.

11. A process according to any one of claims 8 to 10, in which the first liquid feed to the secondary esterification zone (or to the first such zone, if more than two secondary esterification zones are used) comprises a mixture of monoesters (i.e. monoalkyl maleate and monoalkyl fumarate) and diesters (i.e. dialkyl maleate and dialkyl fumarate).

12. A process according to claim 11, in which said mixture of monoesters and diesters is obtained by passage of the monoesterification product mixture possibly after admixture of further alkanol therewith, through a primary esterification zone containing a charge of a solid esterification catalyst.

13. A process according to claim 12, in which at least a major part of the water of esterification present in the primary esterification product is removed therefrom by distillation, to yield an ester feedstock which is used as the first liquid feed to the secondary esterification zone, or to the first of a plurality of such zones connected in series.

14. A process according to any one of claims 8 to 13, in which the second feed stream comprising said alkanol is supplied in liquid form to the, or to each, secondary esterification zone and vaporised therein.

15. A process according to any one of claims 8 to 13, in which the second feed stream comprising said alkanol is

supplied in vapour form to the, or to each, secondary esterification zone.

16. A process according to any one of claims 8 to 15, in which the rate of supply of the second feed stream comprising said alkanol as, or to form, the vaporous stream in the or each secondary esterification zone is such as to establish and maintain a sufficient concentration of reactant alkanol in the liquid phase to drive the mono- to dialkyl maleate and fumarate esterification reactions towards completion and to strip a major part of the water of esterification released by means of these reactions in the respective secondary esterification zone from the liquid phase.

17. A process according to claim 16, in which a second feed stream comprising "dry" alkanol is used with a water content of about 1 mole % or less, and in which the liquid product stream comprises at least about 95 mole % of a mixture of dialkyl maleate and dialkyl fumarate.

18. A process according to claim 16, in which the water content of the second feed stream is about 10 mole %, and the diester content of the liquid product stream is about 80 mole % up to about 85 mole %.

19. A process according to any one of claims 1 to 18, in which a mixture of acidic residue and maleic anhydride is used, which contains at least about 50 mole % of acidic residue and not more than about 50 mole % of maleic anhydride.

Published 1988 at The Patent Office, State House, 66 71 High Holborn, London WC1R 4TP. Further copies may be obtained from The Patent Office. Sales Branch, St Mary Cray, Orpington, Kent BR5 3RD. Printed by Multiplex techniques ltd, St Mary Cray, Kent. Con 1/87